



# Electrical characterization and water sensitivity of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ as a possible solid oxide fuel cell electrode

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## HIGHLIGHTS

- Synthesized  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  by combustion synthesis.
- Electrical conductivity measured on porous samples.
- $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  reacts with  $\text{H}_2\text{O}$  at low temperatures.
- Lack of stability of  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  is an impediment to its incorporation in fuel cells.

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## ABSTRACT

$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SFMO) powders were synthesized by combustion synthesis. Porous samples were formed by uniaxial pressing of powder compacts and sintering in air. Electrical conductivity was measured by a four-point DC technique over a temperature range from 200 °C to 800 °C in air and in hydrogen. Crystal structures were investigated by X-ray diffractometry. Stability of powder samples was investigated in  $\text{H}_2\text{O}$ -containing atmospheres. It was observed that  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  was stable at 800 °C in water-containing atmospheres. However, it reacts with water at low temperatures. Reaction of  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SFMO) with water at low temperatures is a potential shortcoming of this material for application in solid oxide fuel cells (SOFC) due to concerns regarding degradation of the electrodes at low temperatures during cycling.

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## 1. Introduction

Many perovskite materials containing transition metal ions are known to be mixed ionic–electronic conductors. Examples include Sr-doped  $\text{LaFeO}_3$  (LSF), Sr-doped  $\text{LaCoO}_3$  (LSC), Sr-doped  $\text{La}(\text{Co,Fe})\text{O}_3$  (LSCF) and similar compounds [1–3]. Several perovskites also exhibit order-disorder transitions when either the A and/or the B site contains ions of different valences. In the ordered state, they may form double or triple perovskites. Some of the examples of materials exhibiting order-disorder phenomena include ferroic materials such as lead scandium tantalate (PST) and lead magnesium niobate [4,5]. One of the perovskite materials that has been extensively studied is  $\text{Sr}_2\text{FeMoO}_6$  (SFMO), in which Fe and Mo exhibit order leading to a double perovskite unit cell. By virtue of the presence of iron, this material is known to exhibit many

interesting electronic and magnetic properties [6]. For example, SFMO exhibits colossal magnetoresistance (CMR), tunneling magnetoresistance across grain boundaries, and a high Curie temperature ( $\sim 415$  K). Recent investigations have focused on applications in spintronics and in plasmonics [7–10].

Similar to many other perovskites, SFMO exists over a considerable range of stoichiometries leading to varied properties. For example, this material can also be fabricated with excess Fe and deficient Mo, such as  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ . Excess Fe and deficient Mo are compensated for by the creation of electronic defects and oxygen vacancies. As such, it is an ideal candidate as a mixed ionic electronic conductor (MIEC). Recent work has shown that it functions well as both a cathode and an anode in solid oxide fuel cells (SOFC), indicating that it exhibits good electrical transport properties and catalytic activity in oxidizing and reducing atmospheres [11,12]. Electrical conductivity was also measured in both oxidizing and reducing atmospheres [11,12]. Measurements of electrical conductivity were made on sintered, bulk samples, which is the standard procedure used in most studies.

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While SFMO exhibits interesting properties for potential application in SOFCs, there are several references which have reported instability of SFMO under various conditions. It has been reported that SFMO has a narrow  $pO_2$  window of stability, between  $(-9.8 \geq \log pO_2 \geq -13.5)$  at 1200 °C [13]. In another study, similar results were obtained in which a  $pO_2$  stability range between  $(-10.2 \leq \log pO_2 \leq -13.7)$  at 1200 °C was reported [14]. It was also reported that SFMO reacts with water, to the extent that total decomposition occurs when in contact with water [15]. Other investigators determined that SFMO is unstable over time in air at temperatures greater than 400 °C, and that it quickly disintegrates into  $SrMoO_4$  and  $SrFeO_{3-x}$  [16]. Yet another study found a sign change in the temperature coefficient of resistivity of SFMO. These authors proposed that growth of an insulating layer occurs at the grain boundaries [17]. Finally, SFMO has been reported to be unstable even at room temperature in air, leading to unit cell expansion over time promoting phase decomposition [18].

The objective of the present study was to investigate electrical conductivity on porous samples of SFMO as a function of temperature and in various atmospheres. The reasons for making measurements on porous samples are threefold. First, from a practical standpoint, measurements made on porous samples are directly applicable to the design of SOFC electrodes, which are porous. Second, from a fundamental standpoint, measurements made on porous samples allow the determination of properties under thermodynamically equilibrated conditions [19,20]. This is because thermodynamic equilibration occurs orders of magnitude faster in porous samples than in sintered, bulk samples due to fast gas phase equilibration in porous interstices and rapid solid-state equilibration in micron-sized particles [19,20]. This allows measurements under thermodynamically equilibrated conditions at exceptionally low temperatures. For example, our previous work on Sm-doped  $CeO_2$  (SDC) demonstrated rapid equilibration in porous samples at temperatures as low as 200 °C [20]. The work on porous SDC samples demonstrated that the electrolytic domain of SDC at 400 °C was much narrower than previously believed [20]. Also, any possible reactivity of a material with atmosphere can be investigated in a reasonable period of time on porous samples unlike measurements on dense samples. Such reactivity will most certainly occur in the actual devices because of the use of porous electrodes, but may not become noticeable when measurements are made on dense samples. Third, the presence of alkaline earth (here, Sr) increases the potential for reaction with water-containing atmospheres, especially at low temperatures, which can be studied more conveniently and in a reasonable period of time on porous samples than on dense samples. It is known, for example, that many inorganic oxides containing either alkali (Na, K, etc.) or alkaline earth (Ba, Ca, Sr, etc.) metals react with water at low temperatures to form the corresponding bases.

For over two decades,  $Sr_2FeMoO_6$  (SFMO) has been investigated for applications in magnetic storage, read/write heads and similar devices. The current commercial status, however, has not yet gone beyond prototype devices due in part to the instability of the material. The objective of the present study was to investigate properties of porous SFMO over a wide range of temperatures and assess the implications concerning its water sensitivity for applications in SOFC.

## 2. Experimental procedure

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$  (SFMO) powder was synthesized using the following procedure. Stoichiometric amounts of  $Sr(NO_3)_2$  and  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  were dissolved into distilled water to form an aqueous solution. Glycine (0.5 mol glycine per mol of  $NO_3^-$ ) and citric acid (0.05 mol citric acid per mol of  $NO_3^-$ ) were subsequently

added to the solution as a binder and as a pH adjuster.  $Fe(NO_3)_3 \cdot 9H_2O$  was then added in the solution and a dark reddish solution was eventually obtained. The solution was then heated in a microwave oven until self-ignition occurred. The ash was collected and calcined at 1000 °C for 5 h. The as-synthesized powder was mixed with 15% Spheron 6 carbon (by weight). Carbon was added to ensure that the sintered samples exhibit some open porosity. Bars of cross-sections 3 mm × 10 mm and 3 mm × 6 mm were die-pressed. The bars were heated in air in a furnace to 1200 °C for 2 h, and then cooled to room temperature. Platinum paste (ESL Electroscience, Type 5542 Print GD) was applied in the form of four stripes on the samples to form contacts for four-probe conductivity measurements. The samples were then heated to 900 °C to bond the platinum contacts to the  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$  sample surface. Platinum wires were then attached to the four contacts. The samples were inserted into a Barnstead Thermolyne 21100 tube furnace. The ends of the tube were fitted with rubber stoppers and all feed-throughs were inserted through the rubber stoppers. Keithley 2000 multimeters were used for voltage and current measurements. A zirconia oxygen sensor (CoorsTek) was used to measure the oxygen partial pressure inside the tube close to the sample. The temperature inside the tube furnace was monitored using Omega Engineering Type K thermocouple (Omega part # CHAL-020). Cylinders of UHP hydrogen, 10% hydrogen – 90% nitrogen, and compressed air were used to vary the atmosphere inside the tube furnace.

Constant, regulated current (usually < 15 mA) was supplied to the sample using a Keithley 6220 precision current source, and monitored with another Keithley 2000 multimeter. The four Keithley 2000 multimeters were monitored using LabView software on a PC. For each atmosphere investigated, the temperature was varied between 800 °C and 200 °C in 100° steps. Initially, the sample/furnace was heated to 800 °C and the sample conductivity was measured. Thereafter, the temperature was lowered to 200 °C in 100° steps. At each temperature, the conductivity was measured after the sample temperature had equilibrated. Prior work has shown that the kinetics of thermodynamic equilibration of porous samples under imposed conditions is very rapid as long as the material is stable under conditions [20]. Thus, as soon as temperature has equilibrated, the sample thermodynamically equilibrates rapidly [20]. After the measurement at 200 °C, the sample was reheated to 800 °C and the procedure was repeated. These two repetitions are labeled “1st expt” and “2nd expt” in the figures. Each step was approximately 8 h long. Only one data point (800 °C) in 10%  $H_2$  could be obtained as the sample failed during testing. It is speculated that reaction products formed on the surfaces of exposed particles of porous SFMO led to volume changes, which resulted in cracking of the sample.

After the testing was complete, the sample was removed from the furnace. It was observed that the sample had fractured into a few pieces. The fragments were examined by XRD and SEM. Another sample was selected for Archimedes density measurement. The sample was weighed dry in air, weighed while submerged in water and weighed in air after boiling in water and wiping off surface water. The as-synthesized powder was also submerged in water for 3 days. The powder was then removed, dried in a Lindberg/Blue M oven at 50 °C, and heated to 800 °C in air for 24 h. The powder was weighed after each step.

## 3. Results and discussion

Fig. 1 shows an XRD trace of the as-synthesized SFMO powder obtained with  $CuK\alpha$  radiation. The trace is consistent with single phase SFMO of the double perovskite structure with a lattice parameter of 0.7826 nm. Fig. 2 shows the measured DC four probe

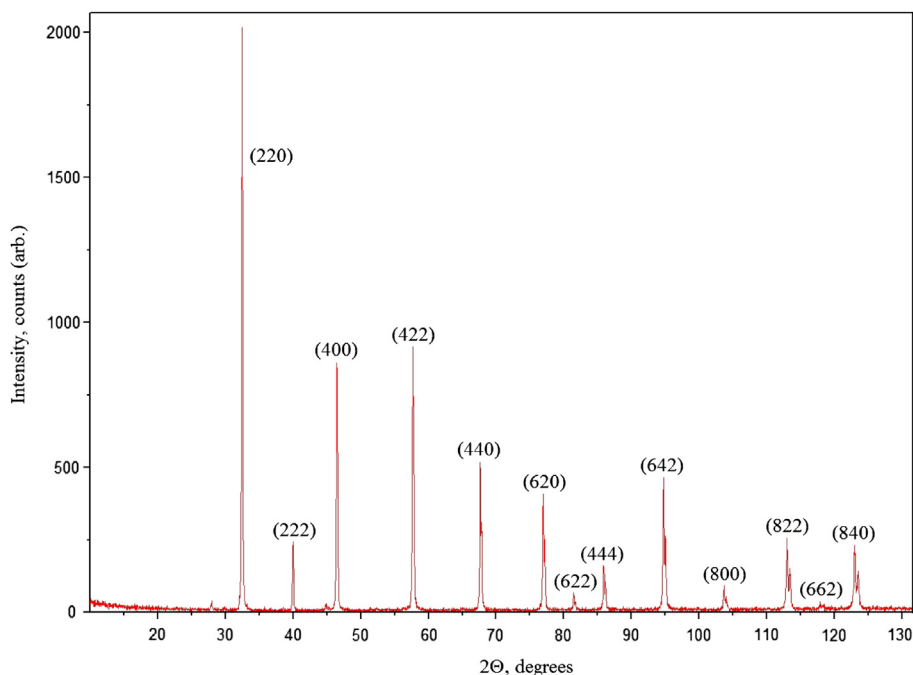


Fig. 1. An XRD trace of the as-synthesized  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SFMO) powder.

conductivity of a sample as a function of temperature on an Arrhenius plot over a temperature range between 200 °C and 800 °C. The red and black squares (in the web version) correspond, respectively, to measurements made during the first and the second run, both in 100%  $\text{H}_2$  atmosphere, during cooling from 800 °C to 200 °C in 100° steps. It was observed that during the second run, the measured conductivity was considerably lower than during the first run, especially at lower temperatures. Triangles and crosses in Fig. 2, respectively, correspond to measurements made during the first and the second run in air. Greater deviation is observed at higher temperatures, although the trends are not so clear in these sets of measurements.

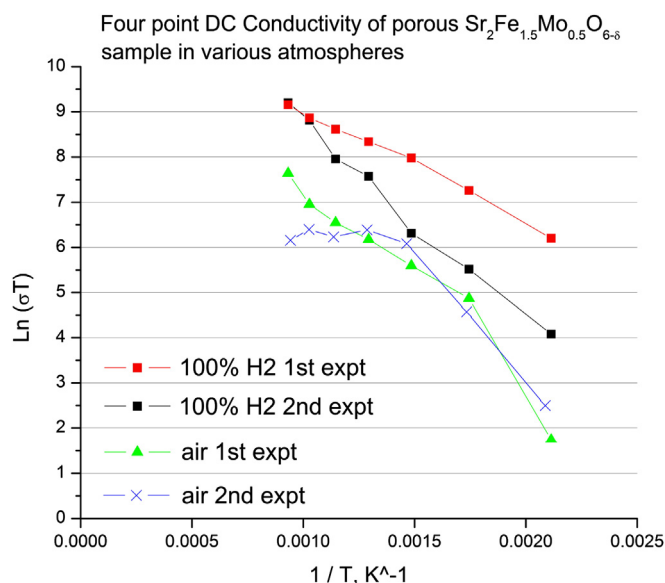


Fig. 2. An Arrhenius plot of conductivity vs. temperature measured on a porous SFMO sample in hydrogen and in air during two consecutive experiments.

Fig. 3 shows the measured conductivity as a function of time for the measurements made in hydrogen. Also plotted in the figure is the temperature vs. time trace for the two runs as the temperature was varied between 800 °C and 200 °C. Note that stable conductivity values were recorded during the first run from 800 °C to 200 °C at each temperature. However, when the sample was reheated to 800 °C during the second run, stable conductivity value was not achieved over the period the sample was maintained at 800 °C (about 8 h). The conductivity increased over the duration of this step. This observation suggests that some instability (reaction) occurred at low temperatures, and some changes in the material

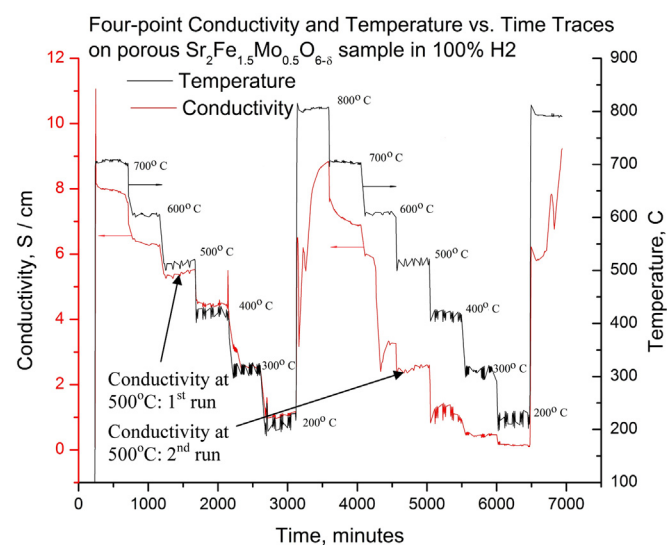


Fig. 3. Conductivity vs. time for measurements over a range of temperatures between 800 °C and 200 °C during two consecutive experiments. Also plotted in the figure is the corresponding temperature vs. time plot. Note that during the second run, stable values of conductivity were not observed. This is attributed to the reaction of SFMO with moisture at low temperatures.

continued to occur when the sample was heated to 800 °C. Stable values of conductivity were not observed during the second run as seen in Fig. 3. The corresponding data for the two runs are shown as squares in Fig. 2. At the end of conductivity measurements, an XRD trace of the sample was obtained. The two XRD traces of the sample, before and after testing, are compared in Fig. 4. The same XRD peaks are present in both spectra, although some peak broadening seems to have occurred in the sample after testing. The absence of detectable amounts of reaction products in the XRD trace after conductivity tests is attributed to relatively sluggish reaction kinetics when H<sub>2</sub>O is present in a vapor form such as at 200 °C. Under such conditions, any water soluble reaction product (e.g. Sr(OH)<sub>2</sub>) cannot be removed thus slowing down kinetics. Similar conductivity measurements on porous SDC showed very stable and reproducible values during heating and cooling, consistent with the fact that the SDC is stable over the range of temperatures and atmospheres tested [20].

A sample of porous sintered SFMO was boiled in water for the measurement of density. Fig. 5 shows photographs of the sample before and after boiling. The pristine sample was black in color. However, after boiling in water, the sample color had changed to brick red. Such a change in color is consistent with Fe<sup>2+</sup> to Fe<sup>3+</sup> transition. XRD traces of the sample before and after boiling are shown in Fig. 6. As clearly seen in the XRD traces, additional XRD peaks were observed in the as-boiled sample. These additional peaks could be identified as belonging to Fe<sub>3</sub>O<sub>4</sub>, SrMoO<sub>4</sub> and SrO<sub>2</sub>. No further characterization tests were conducted to determine if indeed SrO<sub>2</sub> was formed. It is nevertheless clear that SFMO readily reacts with water when boiled for just a few minutes. When boiled in water, soluble reaction products such as Sr(OH)<sub>2</sub> can be continuously removed from the reaction sites thus increasing the kinetics of the reaction. Indeed, similar differences in the kinetics of reaction of H<sub>2</sub>O with alkaline earth cerates have been observed between liquid H<sub>2</sub>O and vapor H<sub>2</sub>O [21,22].

In order to further study reactivity of SFMO with water, a powder sample (0.5001 g) placed in a crucible was immersed in water and maintained for 3 days. After 3 days, the crucible was placed in

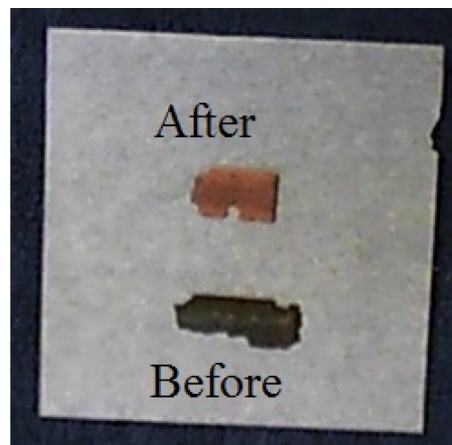


Fig. 5. A photograph of the two halves of the same sample before and after boiling in water for ~20 min. After boiling, the color changed from black to brick red. Sample broke into many pieces during boiling. [For interpretation of color referred in this figure legend, the reader is referred to web version of the article.]

an oven at 50 °C until the powder was fully dry. The crucible contained dry powder at the bottom and some condensate on the sides of the crucible. The color of the powder had changed from black to red. The crucible with the powder was again weighed. The corresponding weight of the powder + condensate was measured to be 0.6718 g, showing a significant increase in weight. The condensate from the crucible walls was removed and weighed. The weight of the condensate was 0.0608 g. The remaining powder was heated to 800 °C in air, maintained at temperature for 24 h, and then cooled to room temperature. The weight of the powder after this heat treatment was measured to be 0.5613 g; which is still greater than the initial weight of the powder. This experiment showed that a significant increase in weight occurred when treated in water. It also showed that heat treatment at 800 °C was not sufficient for solid-state reactions to occur. This is evidenced by the observation that even after treatment at 800 °C, the powder weight (0.5613 g) was

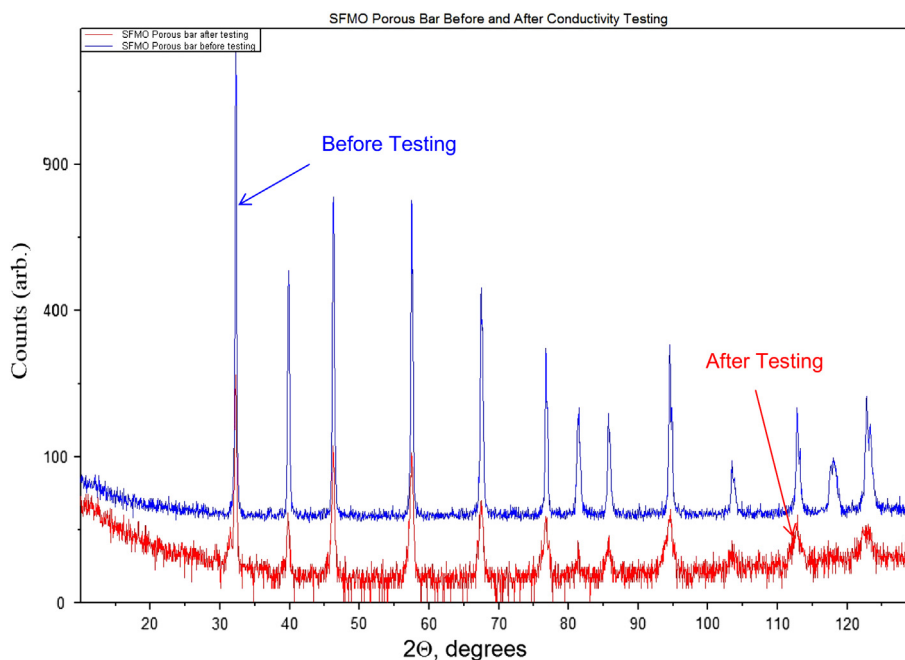
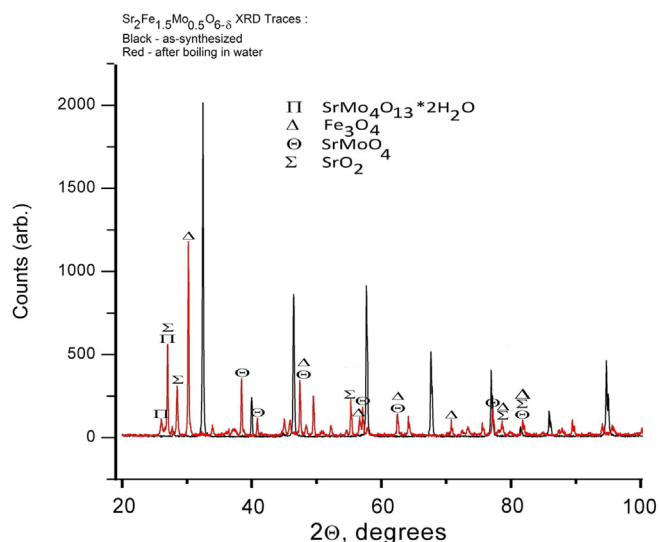


Fig. 4. XRD traces of the as-fabricated porous SFMO sample after several conductivity measurements. The traces appear to be very similar. Small amounts of reaction products, such as Sr(OH)<sub>2</sub>, cannot be detected by XRD. However, they do affect the conductivity.

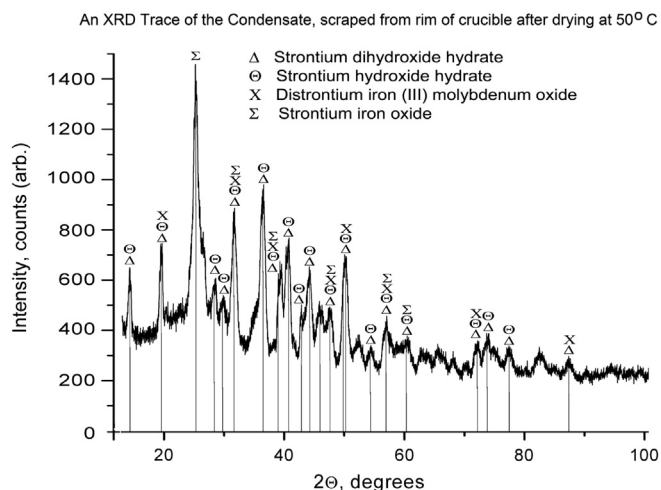




**Fig. 6.** XRD traces of the  $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SFMO) sample before and after boiling in distilled water. Note that boiling in water completely destroyed the original structure and led to the formation  $\text{Sr}(\text{OH})_2$  and other oxides/hydroxides.

greater than the initial weight (0.5001 g), even when the weight of the condensate deposited on crucible walls was excluded. An XRD trace of the condensate deposited on crucible walls is shown in Fig. 7. The observed XRD peaks could be identified with mixed oxides and hydroxides of Sr, Fe and Mo. No further characterization was conducted. However, the instability of SFMO in water-containing atmospheres at low temperatures was clearly documented. Instability of SFMO in water-containing atmospheres is not surprising. It is indeed well known that many oxides containing alkaline earth elements react with water to form highly basic alkaline earth hydroxides. Thus, the observed reactivity of SFMO with water is in accord with expectations.

No thermodynamic data are available for SFMO to the authors' knowledge. However, it is known that  $\text{Sr}_2\text{TiO}_4$  is unstable in water and readily reacts with  $\text{H}_2\text{O}$  to form  $\text{SrTiO}_3$  and  $\text{Sr}(\text{OH})_2$ , for which thermodynamic data are available [23]. At 300 K, the standard free energy for the reaction  $\text{Sr}_2\text{TiO}_4 + \text{H}_2\text{O} \rightarrow \text{SrTiO}_3 + \text{Sr}(\text{OH})_2$  is  $\Delta G^\circ = -61.2 \text{ kJ mol}^{-1}$  [23]. The corresponding equilibrium activity of  $\text{H}_2\text{O}$ , namely  $a_{\text{H}_2\text{O}}$ , is estimated to be  $\sim 2.2 \times 10^{-11}$ . This means



**Fig. 7.** An XRD trace of the condensate from the rim of the crucible after drying in air at 50 °C. The trace corresponds to a number of Sr-containing hydroxides.

even in a relatively dry atmosphere,  $\text{Sr}_2\text{TiO}_4$  would react with trace amounts of  $\text{H}_2\text{O}$ . This has been experimentally confirmed. In fact, its reactivity with  $\text{H}_2\text{O}$  is put to good use in a patented process for the synthesis of nanosize  $\text{SrTiO}_3$  [24]. By contrast, at 1000 K the standard free energy change for  $\text{Sr}_2\text{TiO}_4 + \text{H}_2\text{O} \rightarrow \text{SrTiO}_3 + \text{Sr}(\text{OH})_2$  is  $\sim -8 \text{ kJ mol}^{-1}$ , which is much smaller than at 300 K [23]. Within the uncertainty limits of the available data, it is clear that little thermodynamic driving force exists at 1000 K for the reaction between  $\text{Sr}_2\text{TiO}_4$  and  $\text{H}_2\text{O}$  to proceed to form  $\text{SrTiO}_3$  and  $\text{Sr}(\text{OH})_2$ . Thus, it is expected that  $\text{Sr}_2\text{TiO}_4$  would be stable in the presence of  $\text{H}_2\text{O}$  at high temperatures but not at low temperatures. The behavior of SFMO appears to be very similar to that of  $\text{Sr}_2\text{TiO}_4$ . One of the products after the reaction of SFMO with water was observed to be  $\text{SrMoO}_4$ . This shows that  $\text{SrMoO}_4$  (on a per O basis), which contains a lower concentration of Sr than SFMO, is stable in contact with water. Thus, the instability of  $\text{Sr}_2\text{TiO}_4$  in water at low temperatures is similar to the instability of SFMO in water; and the stability of  $\text{SrTiO}_3$  in water is similar to the stability of  $\text{SrMoO}_4$  in water.

The present observations have significant implications concerning potential applications of SFMO in SOFC as an electrode. It is expected that if maintained at the operating temperature, typically 800 °C, the cells containing SFMO would exhibit chemical stability, and possibly reasonable performance as has already been demonstrated [11,12]. However, whenever the cells are cooled to room temperature, it is expected that SFMO will react with moisture in the atmosphere. This will lead to the formation of various hydroxides, principally  $\text{Sr}(\text{OH})_2$ . For short term exposures to moisture, such as is present in even dry environments, the formation of trace amounts of  $\text{Sr}(\text{OH})_2$  is expected. This would lead to a decrease in ionic/electronic conductivity and especially decrease in catalytic activity. When heated back to the SOFC operating temperature, which is typically 800 °C, the reaction of  $\text{Sr}(\text{OH})_2$  with Fe–Mo-oxides is not expected to occur in a reasonable period of time due to sluggish kinetics of solid state reactions. Indeed it was observed that after a few hours at 200 °C, the original electrical conductivity at 800 °C could not be recovered in 8 h, as seen in Fig. 3. Much higher temperatures, perhaps 1200 °C, would be required for reforming SFMO. Such a high temperature treatment is not possible with any of the SOFC components currently in use or under development. Thus, damage developed at low temperatures during thermal cycling is expected to be cumulative. For example, based on the present work, it is expected that once reaction with  $\text{H}_2\text{O}$  vapor occurs on the surfaces of the particles of a porous body, the products will lead to a local increase in volume. This increase in volume cannot be accommodated by any other means than cracking due to the fact that the material is brittle. The observation that after the conductivity measurements the sample cracked into multiple pieces is in accord with expectations. Similar behavior is expected of an SOFC electrode after repeated thermal cycling. The volume change that occurs upon reaction with  $\text{H}_2\text{O}$  will likely lead to electrode cracking or delamination or both. The reactivity of SFMO with water at low temperatures appears to be the principal limitation to its possible application as an SOFC component.

#### 4. Summary

SFMO powder was synthesized by a combustion process. Bar-shaped porous samples were fabricated by sintering and four-probe DC electrical conductivity was measured in air and in hydrogen over a range of temperatures between 200 and 800 °C. Reactivity of SFMO with water was investigated at low temperatures. It was observed that SFMO readily reacted with water to form  $\text{Sr}(\text{OH})_2$ . Upon reheating to 800 °C, the formed  $\text{Sr}(\text{OH})_2$  did not react back to form SFMO. In an SOFC application, it is expected that

damage created at low temperatures during cycling will be cumulative. This imposes severe restrictions on any potential applications of SFMO in fuel cells.

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